Matsumoto (cited)

ABSTRACT

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The biological activity of herbicides (2,4-D and urea-type experimental herbicide) and fungicides (phthalide and amide-type experimental fungicide, etc.) was examined in the presence or absence of humectant (glycerine or sodium lactate). Depending on the concentration or the type of humectant incorporated, the pesticides showed different activities. The effect of humectants on pesticide uptake through plant leaf surfaces is discussed in relati n to the moisture enhancement and water solubility changes of pesticides by incorporating the humectants.

I. INTRODUCTION

Pesticide uptake through plant leaf surfaces has been a great concern for formulation scientists.[8] Studies on the mechanism of pesticide penetration through plant cuticle have been reviewed in the literature.[2,3,6] In those studies, Fick's first law is commonly used for analysis of the mechanism. According to Fick's first law, the concentration of a solute in water outside the cuticular membrane is the driving force for the transcuticular movement.

Figure 1 shows the schematic procedure of pesticide uptake through plant leaf surfaces. Pesticides repeat drying and wetting effect on the leaf surface after being sprayed. Then, precipitation and dissolution of the pesticide in the retained water takes place. The dissolved part of the pesticide must be used for the successive penetration pathway. Therefore, the function of water retained on the leaf surface is thought to be very important for pesticide uptake.

There have been many reports on pesticide uptake in relation to relative humidity using labeled compounds.[4,5] Humectants have also been examined for uptake studies of pesticides[1,9] or fertilizers.[7,10] However, actual moisture retained in the formulated pesticide has not been precisely examined yet, and the incorporation of humectants sometimes had negative effects on the uptake.

In this chapter, we will discuss (1) the extent to which pesticide activity depends on the retained water (equilibrium moisture), (2) the extent to which humectants enhance the retention of moisture in the pesticides dried after spraying, (3) how actual pesticidal activity may be affected by the incorporation of humectants, and (4) what other side effects will appear by the incorporation of humectants.

II. MATERIALS AND METHODS

A. PESTICIDES

For herbicidal activity tests, 2,4-D [(2,4-dichlorophenoxy)acetic acid] and urea-type experimental herbicide (urea herbicide) were used. The 2,4-D formulation was a 90% soluble powder (SP) which is commercially available (Nissan Chemical Ind., Ltd.). The urea herbicide was formulated in our laboratory into 50% wettable powder (WP), 25% suspension concentrate (SC) and 4% dust (D). The particle size of the active ingredient in WP, SC, and D was 2.7, 3.1, and 2.8 μm, respectively.

For the fungicidal activity test, the following commercial fungicides and amide-type experimental fungicide(amide fungicide) effective against rice sheath blight were used: pencycuron 25% WP (Kumiai Chemical Ind. Co., Ltd.): rice sheath blight; flutolanil 25% WP (Nissan Chemical Ind., Ltd.): rice sheath blight; and phthalide 20% WP (formulated in our laboratory): rice blast.

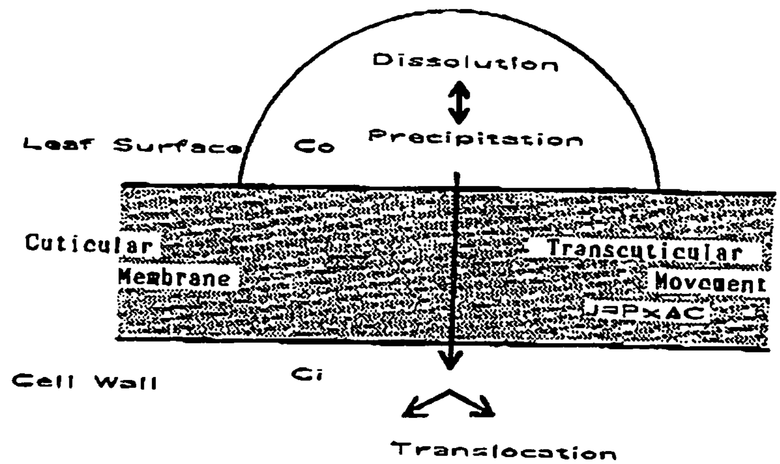


FIGURE 1. Schematic representation of pesticide uptake through plant leaf surfaces.

B. HUMECTANTS

Humectants used for the experiments were glycerine, ethylene glycol, propylene glycol, sodium lactate, polyethylene glycol (mw 400, Toho Chemical Ind. Co., Ltd.), polyvinyl alcohol (GOHSENOL NL-05, Nippon Gohsei Chemical Ind., Ltd.), and sodium polyacrylate (AQUAKEEP 10SH, Seitetsu Chemical Ind., Ltd.).

C. HERBICIDAL ACTIVITY TESTS

1. Effect of Humidity

Three urea herbicide formulations (WP, SC, and D) were used for the herbicidal activity test. Each test solution was sprayed on the leaf surface of common cocklebur (*Xanthium strumarium* L.) (2-leaf stage) and velvetleaf (*Abutilon theophrasti*, Medicus) (3-leaf stage) at doses from 0.19 to 4.0 kg a.i./ha. Treated plants were separately kept for 3 h in the different growth chambers where the humidity was controlled at 20 and 90% RH, respectively. Leaves of the plants were then washed with sufficient water to remove the remaining herbicide on the leaf surface. The test plants were finally moved to the greenhouse and the herbicidal activity was measured 3 weeks after treatment.

2. Effect of Humectants

The urea herbicides WP and 2,4-D were used for this experiment. Each herbicide spray solution was applied on the leaf surface of *X. strumarium* (three-leaf stage) at dosages of 0.125 to 2.0 kg of active ingredient (a.i.) per hectare, with or without humectant (glycerine or sodium lactate) in the spray solution. The amount of humectant added to the spray solution was 0.5 or five times that of each herbicide formulation. The sprayed plants were air dried and then kept in a growth chamber at 70% RH. Herbicidal activity was measured 3 weeks after treatment.

D. FUNGICICAL ACTIVITY TESTS

1. Effect of Humidity

The amide fungicides pencycuron and flutolanil were used for this experiment. Each test solution was sprayed on rice (*Oriza sativa* L.) plant leaves at doses of 20, 40, and 80 g a.i./10A (area unit of a standard Japanese paddy field). The rice plants were separately kept

for 18 h in different growth chambers at 50 and >90% RH, respectively. After washing the leaf surface with sufficient water, the inoculation was carried out by spraying the mycelial suspension of *Rhizoctonia solani*. Fungicidal activity was measured 7 d after inoculation.

2. Effect of Humectants

Spray solutions of phthalide (10, 50, and 100 ppm) were applied on the leaf surface of rice plants (four-leaf stage), with or without humectant (glycerine or sodium lactate) in the solution. After drying by air stream for 1 h, rice plants were kept for 17 h in the growth chamber at >90% RH. The surfaces of the rice leaves were then wiped with acetone-soaked cotton to remove the remaining fungicide on the leaves. Inoculation was carried out by spraying the spore suspension of *Pyricularia orizae*. Fungicidal activity was measured 5 d after inoculation.

E. MOISTURE ANALYSIS

1. Equilibrium Moisture in the Pesticide Dried after Spraying

Three formulations of urea herbicide (WP, SC, and D) were used for this experiment. Each spray solution was dried in an open petri dish for 6 h at 60% RH and 20°C. The moisture content of the residual solid was measured with a Karl Fisher moisturemeter.

2. Effect of Humectants on the Equilibrium Moisture

The WP formulation of the urea herbicide was used for the experiments. The spray solution of the WP containing humectant was air dried for 3 h in an open petri dish. The dish was kept at 20°C in a chamber where humidity was controlled. After 48 h, equilibrium moisture was analyzed with a Karl Fisher moisturemeter. The kind and amount of humectant as well as the humidity of the chamber were changed throughout the series of experiments.

F. WATER SOLUBILITY ANALYSIS

Technical urea herbicide and 2,4-D were used for this experiment. In a 30-ml glass sample tube, 100 mg of technical herbicide and a water solution of humectant were mixed. The sample tube was shaken by a mechanical shaker for 48 h at 25°C. The suspension mixture was then filtered with 0.45-μm plastic paper filter. The concentration of the technical herbicide in the filtrate was analyzed by HPLC. The concentrations of the humectants, glycerine and sodium lactate, in water were changed from 0 to 50%.

III. RESULTS AND DISCUSSION

A. EFFECT OF MOISTURE ON THE BIOLOGICAL ACTIVITY OF PESTICIDES

Moisture effect was examined for fungicides and a herbicide by changing the RH under which sprayed plants were kept for the time necessary for the uptake of pesticides.

Figure 2 shows the effect of moisture on the fungicidal activity of amide fungicide, pencycuron, and flutolanil against rice sheath blight. All three fungicides showed higher activity at higher humidity conditions at any fungicide dosage. The difference in activity between humid conditions and dry conditions was large, especially at lower dosages.

Similar results w re bserved in herbicidal activity tests of the three formulations (D, WP, and SC) of the urea herbicide, as shown in Figure 3: for all three formulations, higher herbicidal activity was observed at higher humidity conditions. In this figure, herbicidal activity is indicated by the mean 90% control dosage (I_{90}) of the herbicide against two weed species (*X. strumarium* and *A. theophrasti*). Therefore, the lower value corresponds to the higher activity.

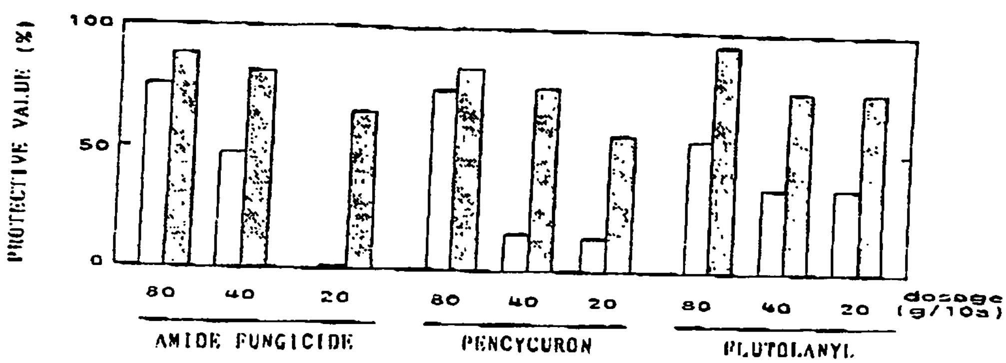


FIGURE 2. Moisture effect on the fungicidal activity of three fungicides (amide fungicide, pencycuron, and flutolanil) against rice sheath blight. White bar, dry condition (RH 50%); shadow bar, humid condition (RO >90%).

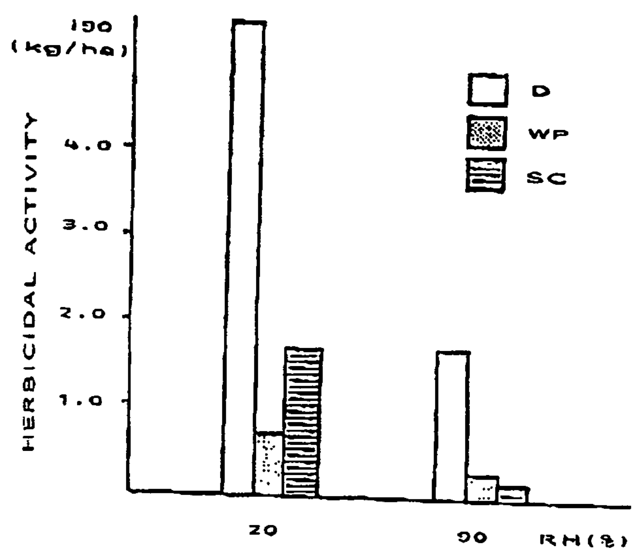


FIGURE 3. Moisture effect on the herbicidal activity of the urea herbicide against two weed species: *Xanthium strumarium* L. and *Abutilon theophrasti* Medicus; formulation types: dust (D), wettable powder (WP), and suspension concentrate (SC); herbicidal activity: mean value of I_{90} against two weeds.

The results of the above two experiments clearly suggest that the moisture level on the leaf surface is very important for pesticide uptake by the plant.

B. EQUILIBRIUM MOISTURE OF SPRAYED PESTICIDES

Figure 3 also indicates the differences in activity among the three formulations at both humidity conditions. The dust formulation showed especially low activity. The particle size of the a.i. in each formulation is almost the same (2.7 to 3.1 μm). Therefore, the difference in activity must be due to other reasons.

The equilibrium moisture of these formulations was measured when the spray solutions were dried at 60% RH and 20°C. The result is shown in Figure 4, in which the dust formulation (D) revealed the lowest amount of equilibrated moisture. This fact could explain the relatively low activity of the dust among the three formulations.

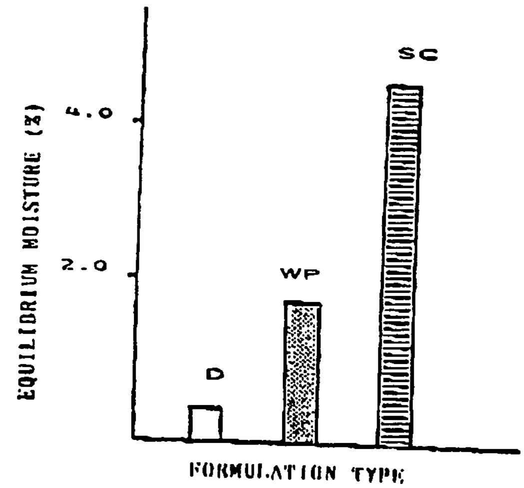


FIGURE 4. Equilibrium moisture content of the three formulations of the urea herbicide when the spray mixture was dried at 60% RH and 20°C. Moisture content measurement: Karl Fisher moisturemeter; formulation types: dust (D), wettable powder (WP), and suspension concentrate (SC).

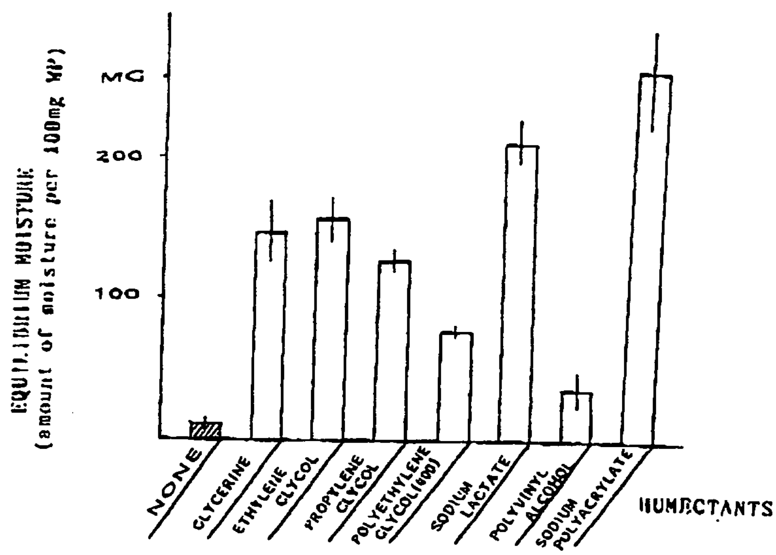


FIGURE 5. Effect of humectants on the equilibrium moisture of the urea herbicide WP formulation when the spray mixture was dried at 90% RH and 20°C.

C. EFFECT OF HUMECTANTS ON THE EQUILIBRIUM MOISTURE

It was suggested in the previous examples that moisture is very important for pesticide uptake (activity). Therefore, adjuvants which may enhance the equilibrium moisture content of pesticides (humectants) were screened.

Figure 5 shows the effect of various humectants on the equilibrium moisture of the urea herbicide (WP formulation) dried under 90% RH when the amount of each humectant added

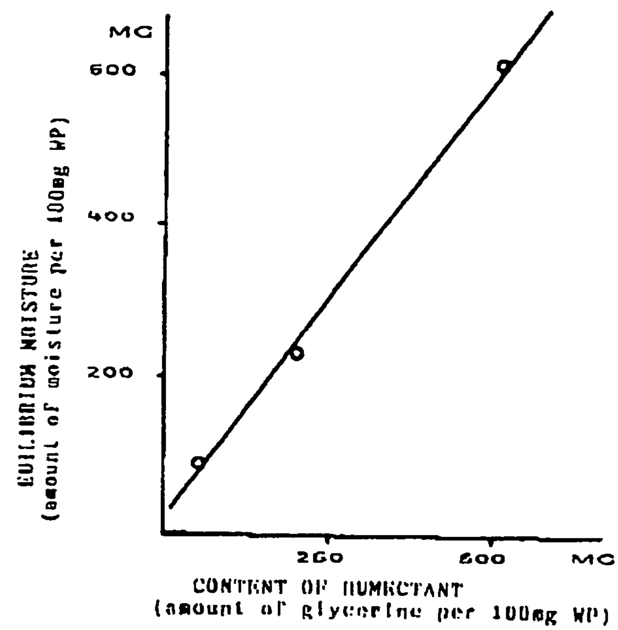


FIGURE 6. Relationship between the amount of humectant added to the spray mixture and the equilibrium moisture of the urea herbicide WP formulation after drying at 90% RH and 20°C.

was half the weight of the WP in the spray solution. Most humectants showed a remarkable enhancement of the equilibrium moisture of the WP. Among these humectants, polyols such as glycerine or ethylene glycol, sodium lactate, and polyacrylate were found to have high moisture-enhancing potency.

Next, the relationship between the amount of humectant added in the spray solution and the equilibrium moisture content in the pesticide was examined using glycerine as a humectant. The result is shown in Figure 6, where we note that the equilibrium moisture increases linearly in proportion to the amount of glycerine.

The equilibrium moisture content of the pesticide was further examined by changing the humidity in the presence or absence of humectants in the spray solution. As shown in Figure 7, incorporation of glycerine into the solution greatly enhances the equilibrium moisture, especially at high humidity conditions.

D. EFFECT OF HUMECTANTS ON THE BIOLOGICAL ACTIVITY OF PESTICIDES

In the previous examples, it was found that humectants have remarkable moisture-enhancing potency. Therefore, their effect on actual biological activity was examined.

Figure 8 shows the fungicidal activity of phthalide against rice blast in the presence or absence of humectants in the spray solution. It was found that both glycerine and sodium lactate increase the activity of phthalide, particularly at lower dosages of the fungicide.

The effect of humectants on herbicidal activity was examined for the urea herbicide and 2,4-D using glycerine and sodium lactate as humectants (Figure 9). In the case of glycerine, both herbicides showed higher activity compared with the case of no humectant. On the other hand, sodium lactate showed almost the same, or rather low, activity compared with the no-humectant case.

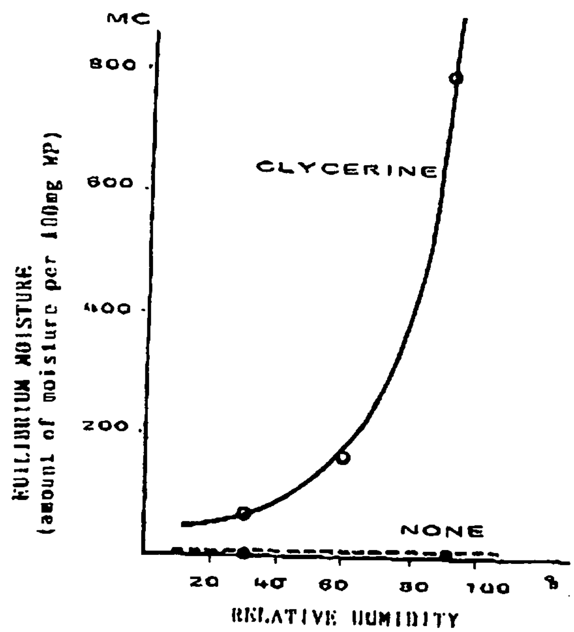


FIGURE 7. Relationship between the humidity and the equilibrium moisture of the urea herbicide WP formulation in the presence or absence of glycerine. Amount of glycerine added to the spray mixture was half the weight of the WP.

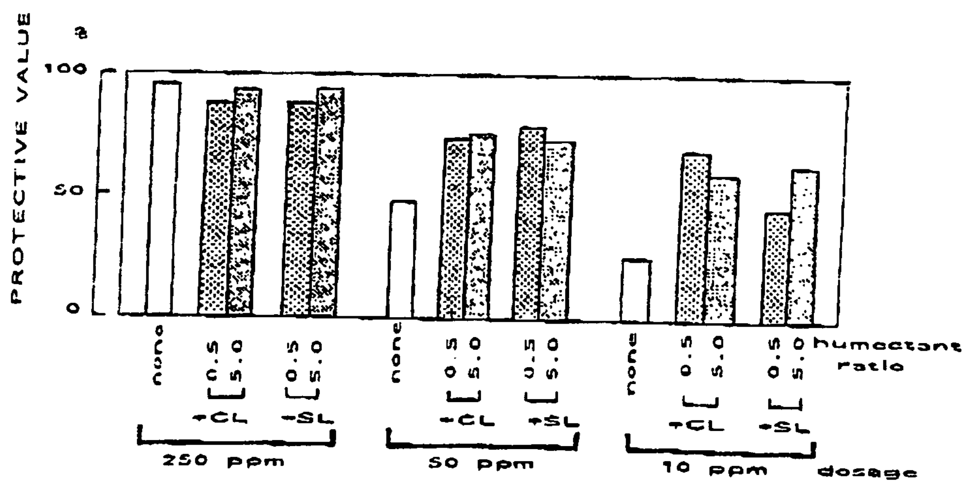


FIGURE 8. Effect of humectants on the fungicidal activity of phthalide against rice blast. +GL, glycerine; +SL, sodium lactate.

The above results with sodium lactate in the herbicidal activity test is inconsistent with the moisture-enhancing potency of this humectant (Figure 5). Therefore, the incorporation of this humectant must result in some factor against activity.

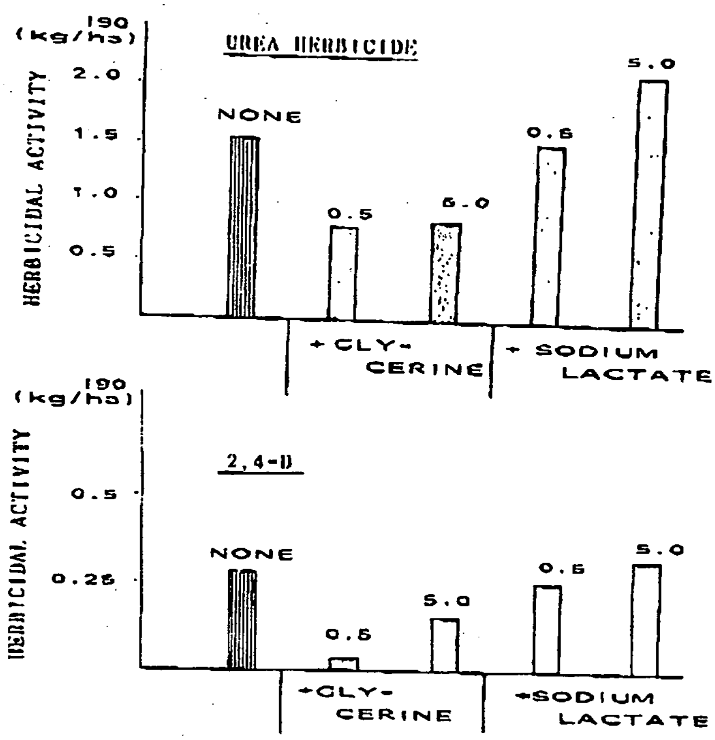


FIGURE 9. Effect of humectants on the herbicidal activity of the urea herbicide and 2,4-D against *Xanthium strumarium* L.

E. OTHER EFFECTS OF HUMECTANTS

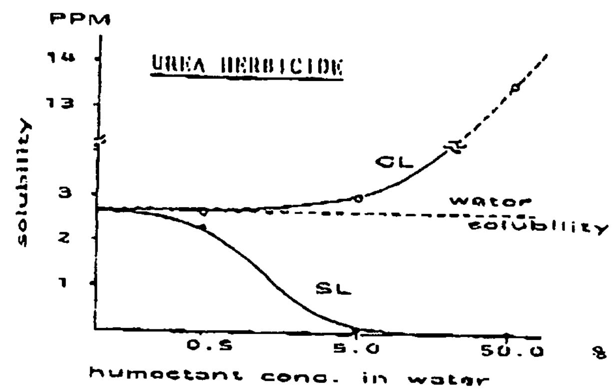
To investigate the cause of the above inconsistency, the solubility change of the previous herbicides in the humectant-water solution was measured by changing the concentration of humectant in the solution.

In the case of glycerine, the solubility of each herbicide keeps almost the same value as the basic water solubility while the humectant concentration increases, although the urea herbicide gradually increases its solubility at high humectant concentrations (Figure 10).

On the other hand, sodium lactate greatly lowers the solubility of both herbicides, particularly at high humectant concentrations. The sprayed pesticide solution will gradually lose water on the leaf surface after spraying. When a humectant is contained in the solution, its concentration will increase in proportion to the water loss of the sprayed solution.

From these considerations, it is thought that one of the reasons for low herbicidal activity in the case of sodium lactate incorporation must be its negative side effect on the solubility of pesticides in the sprayed solution.

There could be some other unknown factors caused by the incorporation of humectants, since all the biological responses which have been shown so far cannot be explained only by the equilibrium moisture or the pesticide solubility change. For example, the relationship between biological activity and the amount of humectant is still unclear. Therefore, further investigation of pesticide uptake in the presence of humectants is necessary.



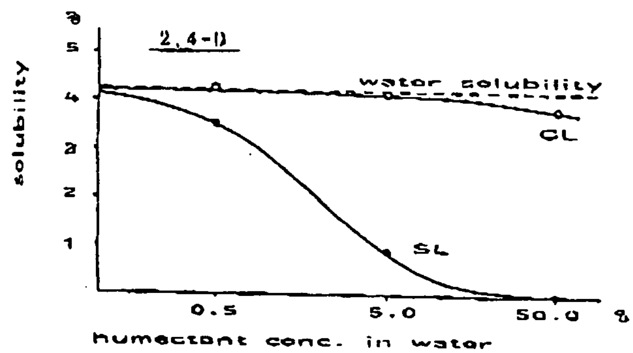


FIGURE 10. Solubility change of the urea herbicide and 2,4-D in the humectant-water solution. GL, glycerine; SL, sodium lactate.

IV. CONCLUSIONS

1. The biological activity of pesticides depends on moisture.
2. Equilibrium moisture retained in the pesticides dried after spraying is affected by the type of formulation.
3. Humectants enhance the retained moisture in pesticides.
4. The solubility of pesticides in the sprayed solution is sometimes affected by the incorporation of humectants.

Moisture enhancement and solubility change by humectants are both important factors for the biological activity (uptake) of pesticides in using humectants as spray adjuvants.

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